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SOLID-LIQUID EQUILIBRIA OF THE TERNARY SYSTEM Na^+, Mg^{++} // Cl^-–H_2O at 10°C

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Abstract

The isothermal section at 10°C of the solubility diagram of the ternary system Na^+, Mg^{++}// Cl^-–H_2O was established by conductimetric and analytical measurements.

Two solid phases, NaCl and $MgCl_2 \cdot 6H_2O$ are observed. The solubility range of NaCl is large, while the liquidus curve of $MgCl_2 \cdot 6H_2O$ is very short.

The composition of the eutonic point, determined by two methods was: 0.32 g% NaCl and 33.80 g% $MgCl_2$.

Keywords: brines, solid-liquid equilibria, solubility

Introduction

The treatment of brines is an important problem for the industrial development of Tunisia since the surface of salt lakes, called 'Chotts' and 'Sebkhats' is very important in the south of the country. Several research projects have been started in the past in order to extract valuable products, but none was completed.

The quinary system involving the major components of brine has been extensively investigated and a compilation of solubility data was prepared about 60 years ago, by d'Ans [1]. Unfortunately the graphical representation of the equilibria [2] is not very convenient for complex systems, so that the use of phase diagrams is very difficult. Moreover, a lot of data cannot be used in the form they are presented in publications:

- they are expressed in various units
- great discrepancies are observed between the results of different authors

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– in spite of their great number, a lot of missing data must be calculated or obtained by extrapolation to the required range of temperature, pressure and composition.

For these reasons the work of collecting and selecting reliable data has been undertaken in the frame of the International Union of Pure and Applied Chemistry (IUPAC commission V. 8). Our laboratory participates in the project and, in order to investigate the possibilities of recovering potassium and/or magnesium salts from brine we have focussed in a first step on the critical evaluation of solubility data for the quarternary system: Na^+, K^+, Mg^{++} / Cl^-–H_2O.

Due to the inaccuracy of data concerning the liquidus surfaces involving magnesium chloride hydrates we had to reinvestigate the ternary system Na^+, Mg^{++} / Cl^-–H_2O. The temperature 10°C was chosen first because it is relevant to the extraction of magnesium salts from the Chott El Jerid, in south Tunisia.

Bibliography

The ternary system Na^+, Mg^{++} / Cl^-–H_2O has been investigated by several authors [3–41], at temperatures between –35°C and 200°C, and more than 950 solubility data are given in the literature. Eight compounds are mentioned: Ice (G), NaCl (N), $NaCl{\cdot}2H_2O$ (N2), $MgCl_2{\cdot}2H_2O$ (M2), $MgCl_2{\cdot}4H_2O$ (M4), $MgCl_2{\cdot}6H_2O$ (M6), $MgCl_2{\cdot}8H_2O$ (M8), and $MgCl_2{\cdot}12H_2O$ (M12). In view to select the best data we have converted the bibliographical data in mole and mass per cent, and reported them on a diagram (Fig. 1). It brings evidence of the big discrepancy between the results from different authors. The solubility ranges of $MgCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}4H_2O$, $MgCl_2{\cdot}8H_2O$, and $MgCl_2{\cdot}12H_2O$ were not determined in the ternary system. The coordinates of the invariant equilibria at constant pressure involving ice, $NaCl{\cdot}2H_2O$, $MgCl_2{\cdot}12H_2O$ (point A), NaCl, $NaCl{\cdot}2H_2O$, $MgCl_2{\cdot}12H_2O$ (point B) were determined; NaCl and $MgCl_2{\cdot}6H_2O$ domains were partially used, but the double saturation points in NaCl and $MgCl_2{\cdot}6H_2O$ are scattered in a cloud, so that the monovariant line could not be drawn.

In general, the composition in $MgCl_2$ can be measured with good accuracy, and the disagreement between the data is due to the small solubility of sodium chloride in saturated solutions of magnesium chloride. For example, for the double saturation solution point in NaCl and $MgCl_2{\cdot}6H_2O$ the given composition in mole% is:

9.26[3] < x_{MgCl_2} < 9.56[23] 0.03[10] < x_{NaCl} < 0.44[3] (17 data) at 25°C
10.11[18] < x_{MgCl_2} < 10.23[26] 0.01[19] < x_{NaCl} < 1.24[18] (4 data) at 55°C

Moreover, the nature of the hydration number of the magnesium salt in equilibrium with liquid is sometimes uncertain since some experimental points are located in regions where other salts are expected to be present.

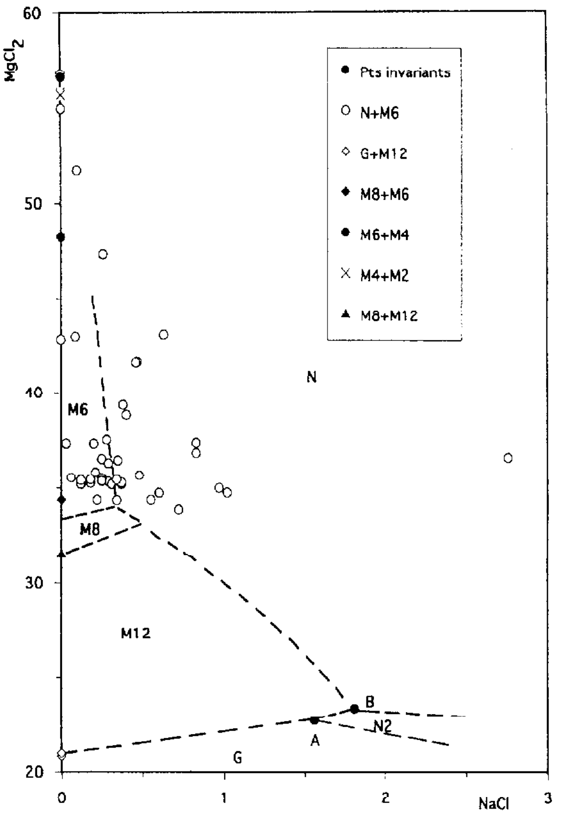

Fig. 1 Ternary system NaCl–$MgCl_2$–H_2O (bibliography)

Experimental techniques

The isothermal section at 10°C of the Na^+, Mg^{++} / Cl^-–H_2O system was established by means of two methods:

Synthetic method

It is based on the variation of the electric conductivity of electrolyte solutions with compositon: small amounts of water are progressively added to a saturated solution of given formal composition, containing an excess of solid. After each addition the conductance is measured when the equilibrium is reached (i.e. when there is no change with time of the conductivity). The curve conductance *vs.* added water is plotted. It presents a break at each phase change, the last one corresponding to the dissolution of the last crystal of salt. The invariant equilibria are characterized by a plateau in the curve.

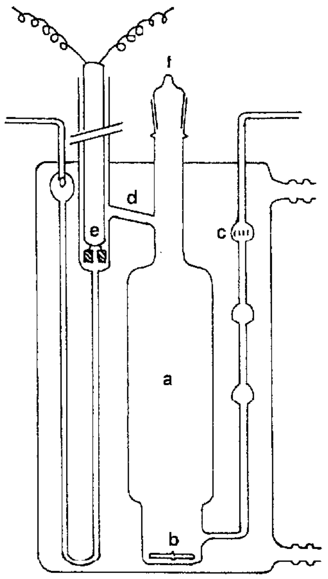

Fig. 2 Experimental device; a – saturation compartment, b – magnetic stirrer, c – sintered glass frit, d – overflow, e– conductivity cell, f – capillary tube

The device used (Fig. 2), built in the laboratory of Physico-Chimie Minérale II, University of Lyon, is composed of a saturation compartment (a) containing the sample. A magnetic stirrer (b) is used to homogenize the mixture. A peristaltic pump ensures a slow circulation of saturated solution through a sintered glassfrit (c) and a lateral outlet. The solution returns in (a) by a U-shaped tube and an oveflow pipe (d). The conductimetric cell (e) is always immersed in saturated solution.

After each determination of conductivity, a small quantity of water (between 0.5 and 1 ml) is introduced in the saturation compartment through a capillary inlet (f) connected to an automatic burette.

The temperature is controlled by means of a thermostatic jacket maintained at 10°C±0.02°C by circulation of water.

Analytical method

The classical 'ensemble' [42] and 'wet residue' [43] methods were used. The mixtures were stirred during one day at constant temperature to attain equilibrium and then allowed to settle. Liquid and solid were then separated and analysed for Na^+, Mg^{++} and Cl^-.

– The sodium content was determined by flame photometry [44].

– Magnesium was determined by titration with EDTA [45]. Eriochrome black II was used as an indicator in ammonia buffer solution (pH=10).

– Chloride was determined by potentiometry [46].

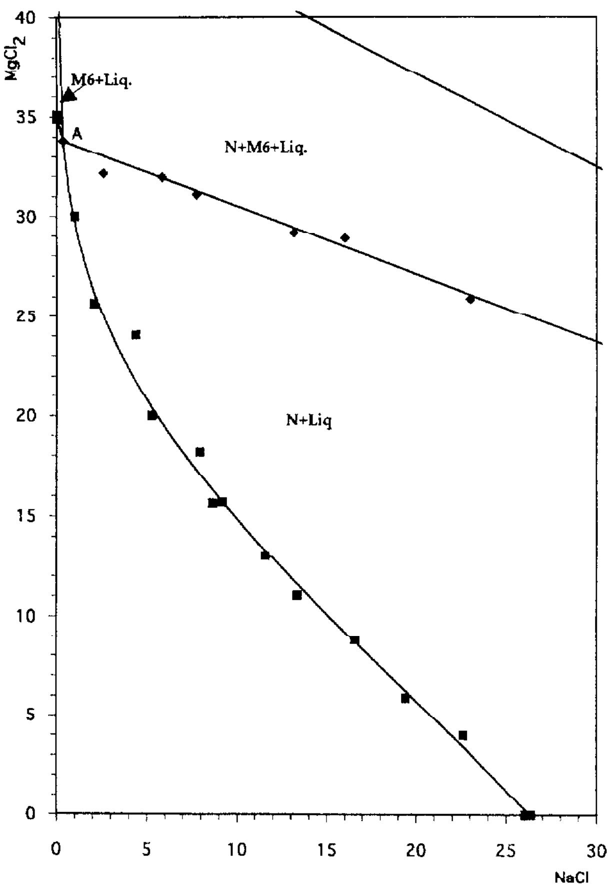

Fig. 3 Isothermal section at 10°C

Compounds

Analytical reagents (99% purity): NaCl, $MgCl_2{\cdot}6H_2O$ were supplied by Merck. $MgCl_2{\cdot}6H_2O$ was dehydrated at 200°C and stored in vacuum in a desiccator over silica gel. Since $MgCl_2$ is highly hygroscopic, we have prepared some mixtures with a saturated solution of $MgCl_2{\cdot}6H_2O$ at 20°C. This had a density of 1.32 and contained 35.28 wt% of $MgCl_2$.

Results

The solubility data are summarized in Fig. 3 and Table 1. They are expressed in mass% (100 w_i) and in mol% (100 x_i) with i=NaCl, $MgCl_2$, water.

At 10°C two solid phases, NaCl and $MgCl_2{\cdot}6H_2O$ are observed. The range of saturation with respect to NaCl is very large while the liquidus curve of

Table 1 Ternary system NaCl–$MgCl_2$–H_2O isothermal section at 10°C

Composition				Solid phases
mass%		mol%		
NaCl	$MgCl_2$	NaCl	$MgCl_2$	
0.00	35.06	0.00	9.27	M6
0.00*	34.90	0.00	9.21	"
0.32	33.80	0.14	8.84	M6+N
1.01	30.00	0.42	7.57	N
2.06	25.66	0.82	6.24	"
4.37	24.04	1.74	5.87	"
5.25	20.00	2.02	4.72	"
7.94	18.19	3.07	4.32	"
8.65	15.64	3.28	3.64	"
9.17	15.69	3.49	3.67	"
11.57	13.04	4.38	3.03	"
13.37	11.05	5.04	2.56	"
16.60	8.80	6.29	2.05	"
19.44	5.89	7.33	1.36	"
22.65	4.00	8.61	0.93	"
26.35	0.00	9.94	0.00	"
26.32**	0.00	9.92	0.00	"

* [4, 26, 29]
** [47]

Table 2 Ternary system NaCl–$MgCl_2$–H_2O section at 10°C, limit of invariant area

Composition				Solid phases
mass%		mol%		
NaCl	$MgCl_2$	NaCl	$MgCl_2$	
0.32	33.80	0.14	8.83	M6+N
2.58	32.17	1.10	8.43	"
5.81	31.97	2.55	8.63	"
7.74	31.12	3.43	8.48	"
13.15	29.20	6.03	8.21	"
16.00	28.93	7.53	8.35	"
22.99	25.92	11.23	7.77	"
33.47	22.44	17.58	7.23	"

$MgCl_2 \cdot 6H_2O$ is very short. An eutonic point is close to the $MgCl_2$ axis. Its composition (0.32 g% NaCl and 33.80 g% $MgCl_2$) was determined by two methods:

– the eutonic point *E* (Fig. 3) is the point of intersection of the liquidus curve of NaCl and of the line joining the representative point of NaCl to E, determined by conductimetric method (Table 2).

– its composition is also given by application of the 'ensemble' and the 'wet residue' methods to mixtures located in the three-phase area of the diagram.

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